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<b>(21) International Application Number:</b> PCT/US96/17521 <b>(22) International Filing Date:</b> 4 November 1996 (04.11.96) <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> UCHIYAMA, Hirotaka [JP/JP]; 5-8-17-3B, Nishiokamoto, Higashinada-ku, Kobe 658 (JP). <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> HAIR CONDITIONING COMPOSITION COMPRISING SILICONE EMULSION  <b>(57) Abstract</b>  Disclosed are hair conditioning compositions comprising a silicone emulsion comprising a silicon polymer selected from the group consisting of a polyalkyl siloxane having a molecular weight of at least 20,000, a polyaryl siloxane having a molecular weight of at least 20,000, an amino-substituted siloxane having a molecular weight of at least 5,000, a silicon resin having a molecular weight of at least 5,000, and mixtures thereof, an anionic surfactant, a compatibilizing surfactant, and a cationic surfactant, wherein the silicone polymer is dispersed as a particle having an average size of not more than 450 nm; a cationic surfactant; and water, wherein the total amount by mole of cationic surfactants in the composition is greater than the total amount by mole of anionic surfactants in the composition.		

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## HAIR CONDITIONING COMPOSITION COMPRISING SILICONE EMULSION

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### TECHNICAL FIELD

The present invention relates to a hair conditioning composition comprising a silicone emulsion.

### BACKGROUND

10 Human hair becomes soiled due to its contact with the surrounding environment and from the sebum secreted by the scalp. The soiling of hair causes it to have a dirty feel and an unattractive appearance. The soiling of the hair necessitates shampooing with frequent regularity.

Shampooing cleans the hair by removing excess soil and sebum. However, shampooing can leave the hair in a wet, tangled, and generally  
15 unmanageable state. Once the hair dries, it is often left in a dry, rough, lusterless, or frizzy condition due to removal of the hair's natural oils and other natural conditioning and moisturizing components. The hair can further be left with increased levels of static upon drying which can interfere with  
20 combing and result in a condition commonly referred to as "fly-away hair", or contribute to an undesirable phenomena of "split ends", particularly for long hair.

A variety of approaches have been developed to alleviate these after-shampoo problems. These approaches range from post-shampoo  
25 application of hair conditioner such as leave-on and rinse-off products, to hair conditioning shampoos which attempt to both cleanse and condition the hair from a single product. Although some consumers prefer the ease and convenience of a shampoo which includes conditioners, a substantial proportion of consumers prefer the more conventional conditioner  
30 formulations which are applied to the hair as a separate step from shampooing, usually subsequent to shampooing. Conditioning formulation can be in the form of rinse-off products or leave-on products, and can be in the form of an emulsion, cream, gel, spray, and mousse. Such consumers who prefer the conventional conditioner formulations value the relatively  
35 higher conditioning effect, or convenience of changing the amount of conditioning depending on the condition of hair or portion of hair.

A common method of providing conditioning benefit to the hair is through the use of hair conditioning agents such as cationic surfactants and polymers, silicone conditioning agents, and hydrocarbon and other organic oils, and solid aliphatics such as fatty alcohols. Cationic surfactants and polymers, as well as oils and aliphatics are known to enhance hair shine and provide moistness, softness, and static control to the hair, however, are also known to provide stickiness or greasy or waxy feeling.

Silicone polymers having high molecular weight are known to provide favorable conditioning benefits such as smoothness and combing ease. However, these high molecular weight silicone polymers tend to have a large particle size and are thermodynamically unstable. Mechanical shearing is known to provide smaller particle size of fluids. High molecular weight silicone polymers are too viscous to emulsify down to a desirable particle size. Thus, high molecular weight silicone polymers could not be formulated at levels that would provide desired conditioning benefits.

A suitable way of obtaining stable, yet high molecular weight silicone polymers are provided by emulsion polymerization of silicone oligomers.

Japanese Patent Laid-open 5-163122 discloses hair cosmetics comprising a dimethylpolysiloxane microemulsion obtained by emulsion polymerization, a dimethylpolysiloxane polyoxyalkylene copolymer, and water. United States Patent 5,504,149 discloses a method for making a silicone emulsion having high viscosity wherein a mixture of water, cyclic siloxane, optional nonionic surfactant and cationic surfactant is polymerized by using silanolate or organosilanolate as an initiator. International Publication WO95/24180 discloses a rinse-off hair conditioning composition comprising a cationic surfactant and an emulsion polymerized dimethiconol nonionic conditioning polymer.

Generally, polymers of high molecular weight relied on the usage of anionic surfactants which act as catalysts for rapid reaction to polymerize the silicone oligomers. Net, the resulting emulsion containing the high molecular weight silicone polymer was in an anionic surfactant-rich condition. This limits the use of the resulting emulsion with cationic conditioning agents, particularly cationic surfactants. Without being bound by theory, it is believed that, if cationic surfactant is directly added to an anionic-rich environment, the anionic surfactants included in the emulsion having opposing ion charges react to destroy the emulsion and/or produce undesired precipitation. This would lead to significant formulation difficulties of high molecular weight

silicone polymers in conditioning composition including certain levels of cationic surfactants. Certain levels of cationic surfactant are known to provide excellent static control to conditioning formulations.

Therefore, there remains a desire to provide a conditioning composition which provides improved conditioning benefits, and is stable with a wide variety of conditioning agents.

In the present invention, a hair conditioning composition comprising a silicone emulsion comprising a high molecular weight silicone polymer made via a certain surfactant system have been developed which provides improved conditioning benefits such as moistness, softness, free flowing, decreased stickiness, and static control, and which can be used with a wide range of conditioning agents.

### SUMMARY

The present invention relates to a hair conditioning composition comprising by weight of the concentrate:

(a) a silicone emulsion comprising:

- i) from about 0.01% to about 20% of the entire composition a silicone polymer selected from the group consisting of a polyalkyl siloxane having a molecular weight of at least 20,000, a polyaryl siloxane having a molecular weight of at least 20,000, an amino-substituted siloxane having a molecular weight of at least 5,000, a silicone resin having a molecular weight of at least 5,000, and mixtures thereof;
  - ii) an anionic surfactant;
  - iii) a compatibilizing surfactant; and
  - iv) a cationic surfactant;
- wherein the silicone polymer is dispersed as a particle having an average size of not more than about 450 nm;

(b) from about 0.1% to about 20% of a cationic surfactant; and

(c) water;

wherein the total amount by mole of cationic surfactants in the composition is greater than the total amount by mole of anionic surfactants in the composition.

Such compositions satisfy the need for a hair conditioning composition which has improved conditioning benefits such as moistness, softness, free flowing, decreased stickiness, and static control, and which can be used with a wide range of conditioning agents.

### DETAILED DESCRIPTION

All percentages herein are by weight of the compositions unless otherwise indicated. All ratios are weight ratios unless otherwise indicated. All percentages, ratios, and levels of ingredients referred to herein are based on the actual amount of the ingredient, and do not include solvents, fillers, or other materials with which the ingredient may be combined as commercially available products, unless otherwise indicated.

The invention hereof can comprise, consist of, or consist essentially of the essential elements described herein as well as any of the preferred or optional ingredients also described herein.

All publications, patent applications, and issued patents mentioned herein are hereby incorporated in their entirety by reference.

#### SILICONE EMULSION

The hair conditioning composition of the present invention comprises a silicone emulsion comprising a silicone polymer, an anionic surfactant; a compatibilizing surfactant, and a cationic surfactant. The silicone emulsion is prepared by emulsion polymerization, wherein an aqueous solution or emulsion of the starting silicone material is mixed with an anionic surfactant, followed by addition of a compatibilizing surfactant, and finally by addition of a cationic surfactant. The starting silicone material is selected so that the resulting silicone polymer in the obtained silicone emulsion has more than a certain molecular weight, and is dispersed as a particle having an average size of not more than about 450 nm, more preferably about from 150 nm to about 250 nm. Silicone polymers having such particle size make a silicone emulsion which is stable with a wide range of components.

A convenient and useful method of preparing the silicone emulsion of the present invention is by utilizing the following procedure:

1) blending a mixture of starting silicone material selected from the group consisting of cyclic silicone oligomers such as cyclic dimethyl siloxanes known as cyclomethicone, mixed silicone hydrolyzates, silanol stopped oligomers, higher molecular weight silicone polymers, functionalized silicones and mixtures thereof with water, and anionic surfactants;

2) heating the blend obtained by mixing the starting silicone material, water and anionic surfactant to a temperature ranging from about 75 to about 98 °C for a period of time ranging from about 1 to about 5 hours;



3) cooling the anionically emulsion polymerized silicone emulsion to temperature ranging from 0 to about 25 °C for a period of time ranging from about 3 hours to about 24 hours;

4) adding a compatibilizing surfactant; and

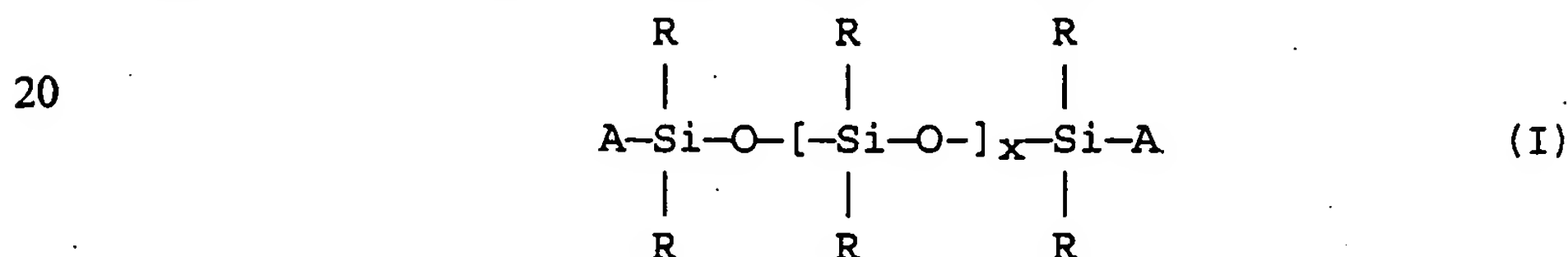
5) adding a cationic surfactant.

The silicone polymer is comprised at a level of from about 0.01% to about 20%, more preferably from about 0.1% to about 10% of the entire composition.

#### Silicone Polymer

The silicone polymer of the present invention are those which provide excellent conditioning benefits to the hair. The silicone polymer is selected from the group consisting of a polyalkyl siloxane having a molecular weight of at least 20,000, a polyaryl siloxane having a molecular weight of at least 20,000, an amino-substituted siloxane having a molecular weight of at least 5,000, a silicone resin having a molecular weight of at least 5,000, and mixtures thereof.

The polyalkyl siloxanes and polyaryl siloxanes useful as silicone polymers herein include those with the following structure (I):

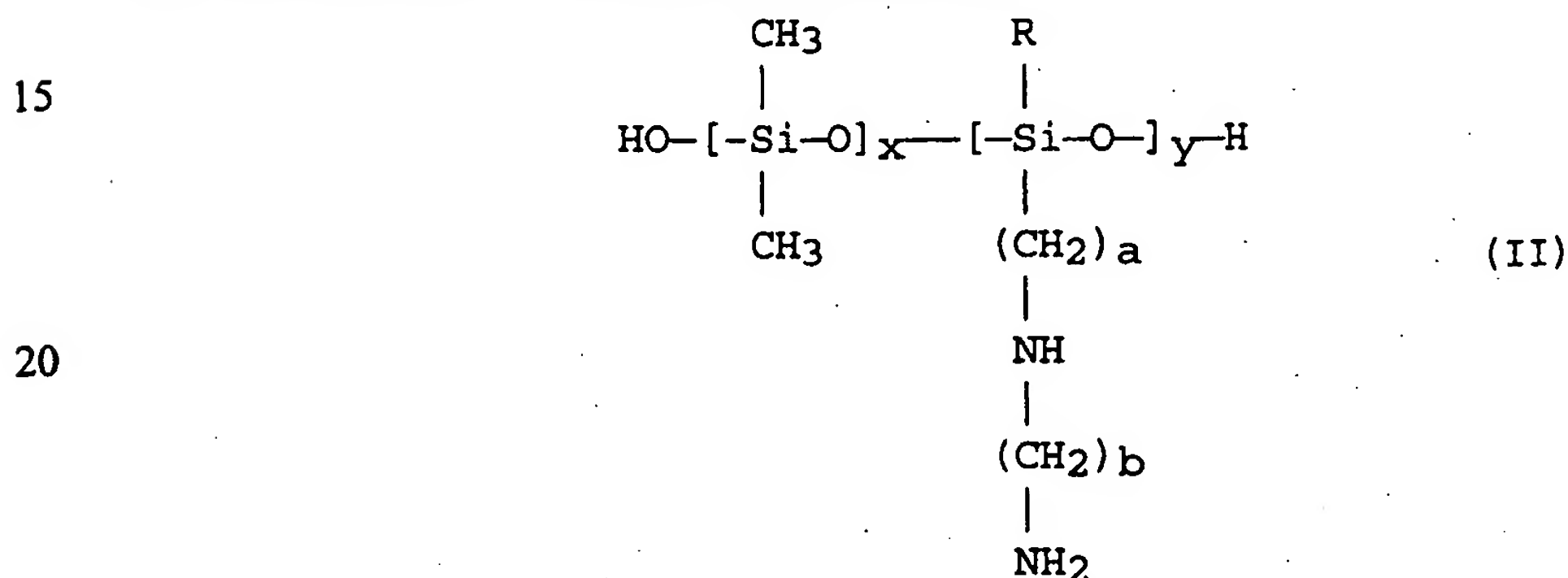


wherein R is alkyl or aryl, and x is an integer from about 200 to about 8,000 having a molecular weight of at least 20,000, more preferably at least 100,000, still more preferably at least 200,000. "A" represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) can have any structure as long as the resulting silicone is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the composition, is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. Suitable A groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicon atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred polyalkyl and polyaryl silicone polymers are polydimethylsiloxane, polydiethylsiloxane,

polymethylphenylsiloxane, and derivatives thereof terminated with hydroxy and carboxyl groups. Polydimethylsiloxane, which is also known as dimethicone, and its hydroxyl terminated derivative, which is also known as dimethiconol, is especially preferred.

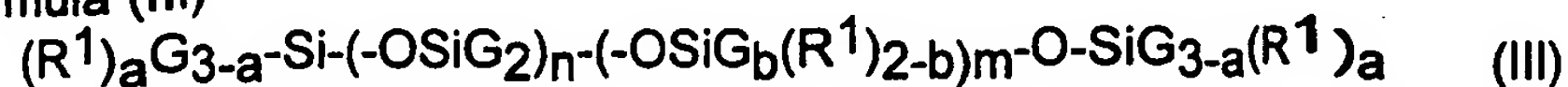
Also useful herein, for enhancing the shine characteristics of hair, are highly arylated silicones, such as highly phenylated polyethyl silicone having refractive indices of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicones are used, they should be mixed with a spreading agent, such as a surfactant or a silicone resin, as described below to decrease the surface tension and enhance the film forming ability of the material.

The amino-substituted siloxanes useful as silicone polymers herein include those with the following structure (II):



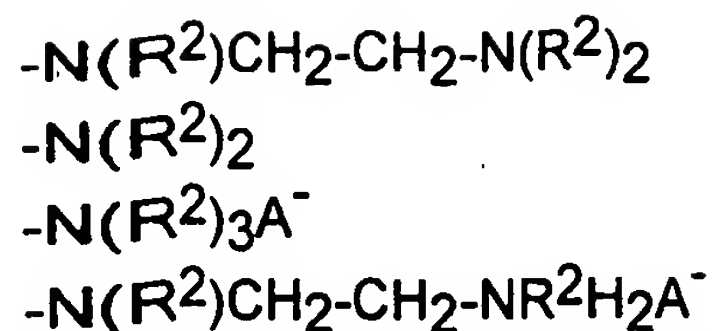
wherein R is CH<sub>3</sub> or OH, x and y are independent integers which depend on the desired molecular weight wherein y is not 0, a and b are independent integers from 1 to 10, and wherein the average molecular weight is at least 5,000, more preferably at least 10,000. This polymer is also known as amodimethicone.

Suitable amino-substituted siloxanes include those represented by the formula (III)



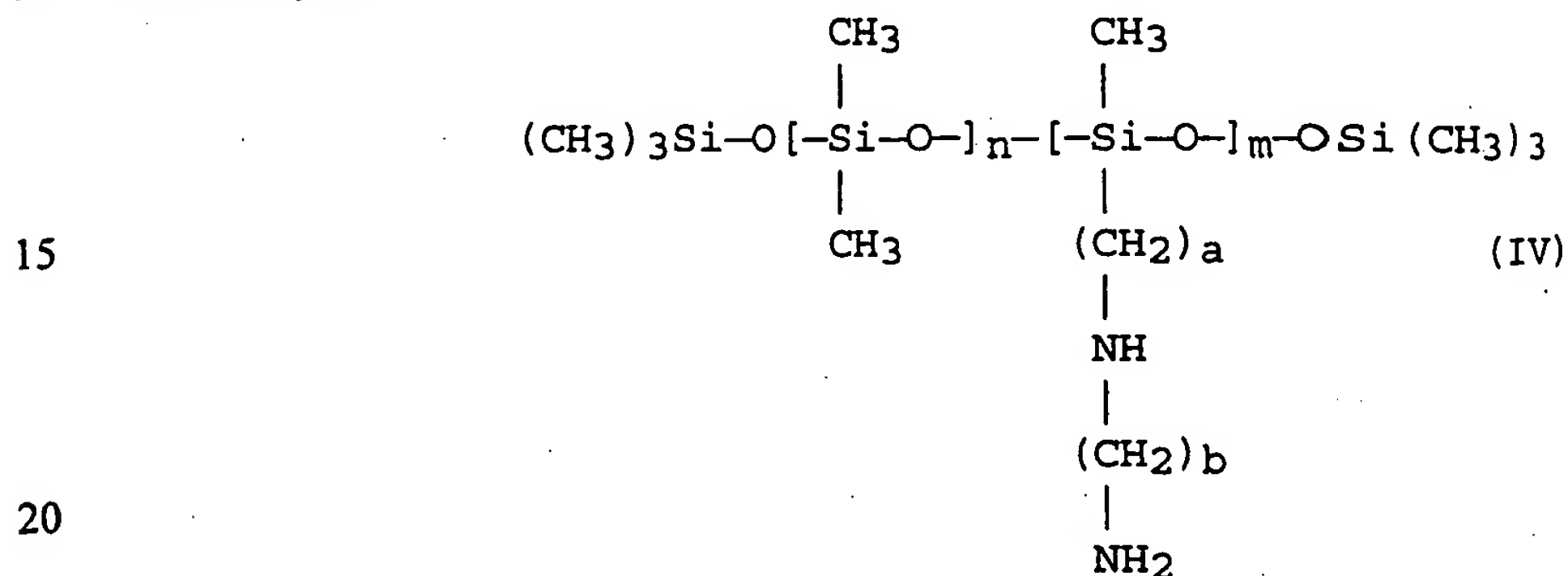
wherein G is chosen from the group consisting of hydrogen, phenyl, OH, C<sub>1</sub>-C<sub>8</sub> alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R<sup>1</sup> is a monovalent radical of formula C<sub>q</sub>H<sub>2q</sub>L in which q is an integer from 2 to 8 and L is chosen from the groups





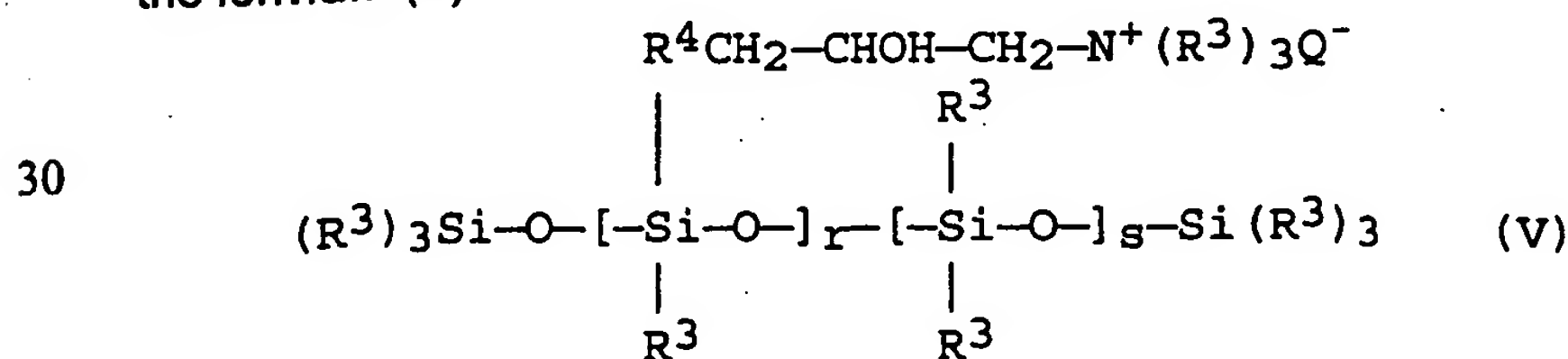
5 in which  $R^2$  is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and  $A^-$  denotes a halide ion.

An especially preferred amino-substituted siloxane corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of  
10 formula (IV):



wherein  $n$  and  $m$  are independent integers of 1 or more selected depending on the desired molecular weight,  $a$  and  $b$  are independent integers from 1 to 10, and wherein the average molecular weight is at least 5,000, more  
25 preferably at least 10,000.

Other amino-substituted siloxanes which can be used are represented by the formula (V):



wherein  $R^3$  denotes a monovalent hydrocarbon radical having from 1 to 18  
35 carbon atoms, preferably an alkyl or alkenyl radical such as methyl;  $R^4$  denotes a hydrocarbon radical, preferably a  $C_1$ - $C_{18}$  alkylene radical or a  $C_1$ - $C_{18}$ , and more preferably  $C_1$ - $C_8$ , alkyleneoxy radical;  $Q^-$  is a halide ion, preferably chloride;  $r$  denotes an average value from 2 to 20, preferably from 2 to 8;  $s$  denotes an average value from 20 to 200, and preferably from 20 to  
40 50.

Also useful are silicone resins, which are highly crosslinked polymeric siloxane systems, having a molecular weight of at least 5,000, preferably at least 10,000. The cross-linking is introduced through the incorporation of trifunctional and tetrafunctional silanes with monofunctional or difunctional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinyl-chlorosilanes, and tetrachlorosilane, with the methyl-substituted silanes being most commonly utilized. Without being bound by theory, it is believed that the silicone resins can enhance deposition of other silicones on the hair and can enhance the glossiness of hair with high refractive index volumes.

Other useful silicone resins are silicone resin powders such as the material given the CTFA designation polymethylsilsequioxane.

Silicone resins can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the monofunctional unit  $(\text{CH}_3)_3\text{SiO}_{0.5}$ ; D denotes the difunctional unit  $(\text{CH}_3)_2\text{SiO}$ ; T denotes the trifunctional unit  $(\text{CH}_3)\text{SiO}_{1.5}$ ; and Q denotes the quadri- or tetra-functional unit  $\text{SiO}_2$ . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone, or an average thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the

MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

- 5 The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0.

Other silicone fluids, gums, and resins can be found in Encyclopedia of  
10 Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989, which is incorporated herein by reference in its entirety.

#### Anionic Surfactant

- 15 The anionic surfactant useful for making the silicone emulsion of the present invention are those which act as an acid catalyst for polymerizing the starting silicone material, and are compatible with the remainder of components. Exemplary anionic surfactants are alkyl sulfonic acids, aryl sulfonic acids, or alkyl aryl sulfonic acids where the alkyl group ranges from one to twenty carbon atoms and the aryl group ranges from six to thirty  
20 atoms. Highly preferable anionic surfactants are those selected from the group consisting of benzene sulfonic acid, xylene sulfonic acid, dodecylbenzene sulfonic acid, and twelve to eighteen carbon atom alkyl group sulfonic acids, and mixtures thereof.

#### Compatibilizing Surfactant

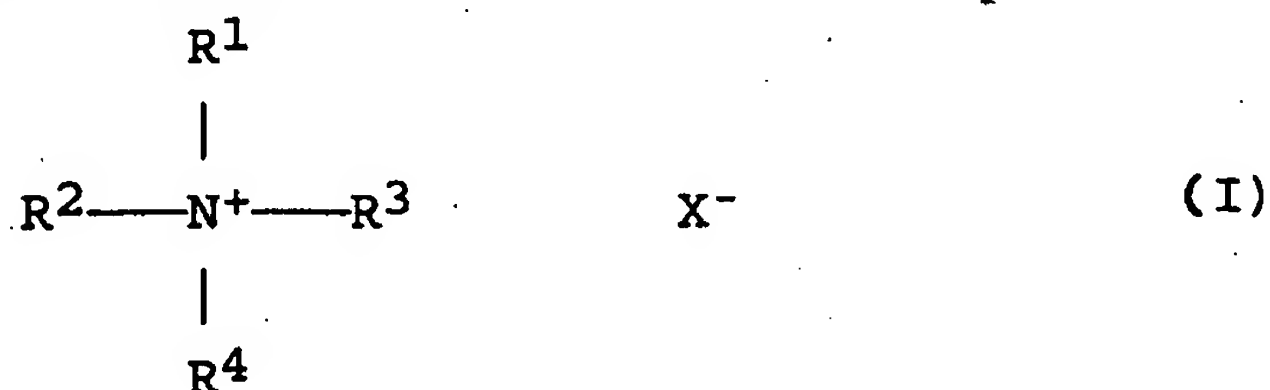
- 25 The compatibilizing surfactant useful for making the silicone emulsion of the present invention are those which function to compatibilize the anionically emulsion polymerized silicone emulsion with the cationic surfactant. Without being bound by theory, it is believed that, if cationic surfactant is directly added to the anionic mixture obtained after the initial emulsion polymerization  
30 of starting silicone material with anionic surfactants, the anionic surfactants included in the anionically emulsion polymerized silicone emulsion having opposing ion charges to the cationic surfactants react to destroy the emulsion and/or produce undesirable precipitation. Thus, the anionically emulsion polymerized silicone emulsion obtained is treated with a compatibilizing  
35 surfactant. Useful compatibilizing surfactants are those having an HLB ratio greater than 9. Particularly useful compatibilizing surfactants are ethoxylated fatty acid esters such as polyglycerin fatty acid esters, polyoxyethylene

sorbitan fatty acid esters, polyoxyethylene castor oils, polyoxyethylene secondary alkyl ethers where the alkyl group ranges from 6 to 40 carbon atoms, polyoxyethylene alkyl ethers where the alkyl group ranges from 6 to 40 carbon atoms, polyoxyethylene alkyl amines where the alkyl groups range from 6 to 40 carbon atoms and may be independently selected, polyoxyethylene alkyl amides where the alkyl groups range from 6 to 40 carbon atoms and the alkyl groups may be independently selected, amphoteric betaine surfactants, and polyoxyethylene lanolins. A particularly preferred group of surfactants are POE(4) lauryl ether, POE(9) lauryl ether, POE(23) lauryl ether, POE(20) stearyl ether, and POE(20) sorbitan mono-palmitate. Another preferred group of surfactants which may be used to compatibilize the anionic emulsion with cationic surfactants is the group consisting of lauryldimethylaminoacetic acid betaine, coco fatty amide propyldimethylaminoacetic acid betaine, 2-alkyl-N-carboxymethyl-N-hydroxyethylimidazolinium betaine, sodium N-lauroyl sarcosine, and lanolin derivatives of quaternary ammonium salts.

#### Cationic Surfactant

Having treated the anionically emulsion polymerized silicone emulsion with a compatibilizing surfactant, the emulsion can be treated with a cationic surfactant to obtain the cationic surfactant containing silicone emulsion of the present invention. Such silicone emulsions are compatible with a wide range of conditioning agents, as well as other components of the composition of the present invention. The cationic surfactants useful for making the silicone emulsion of the present invention are any known to the artisan.

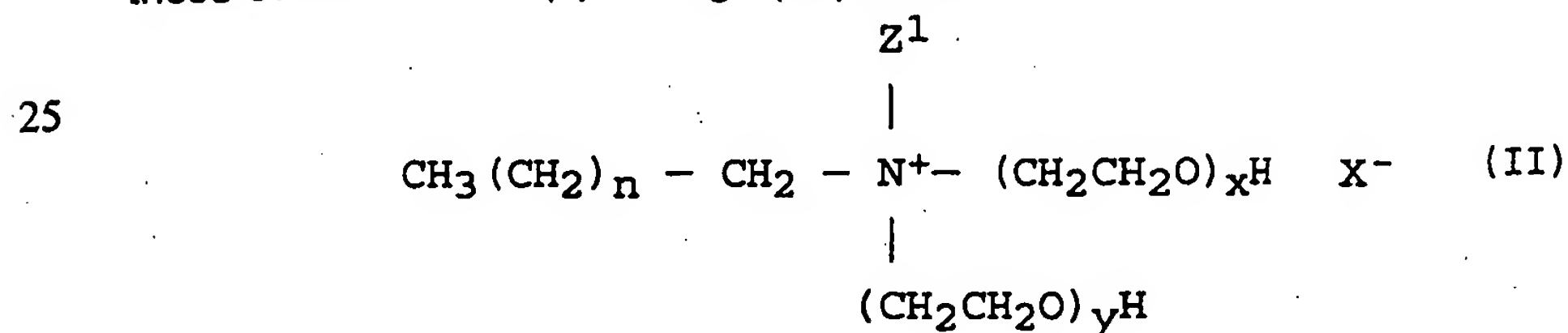
Among the cationic surfactants useful herein are those corresponding to the general formula (I):



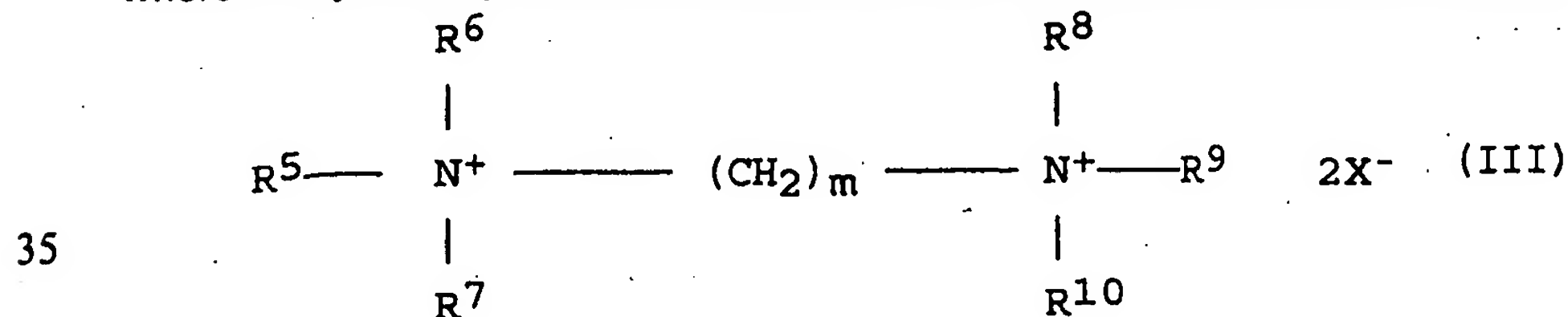
wherein  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are independently selected from an aliphatic group of from 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulfonate, sulfate, alkylsulfate, and alkyl sulfonate

radicals. The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. Preferred is when R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently selected from C<sub>1</sub> to about C<sub>22</sub> alkyl. Nonlimiting examples of cationic surfactants useful in the present invention include the materials having the following CTFA designations: quaternium-8, quaternium-24, quaternium-26, quaternium-27, quaternium-30, quaternium-33, quaternium-43, quaternium-52, quaternium-53, quaternium-56, quaternium-60, quaternium-62, quaternium-70, quaternium-72, quaternium-75, quaternium-77, quaternium-78, quaternium-80, quaternium-81, quaternium-82, quaternium-83, quaternium-84, and mixtures thereof.

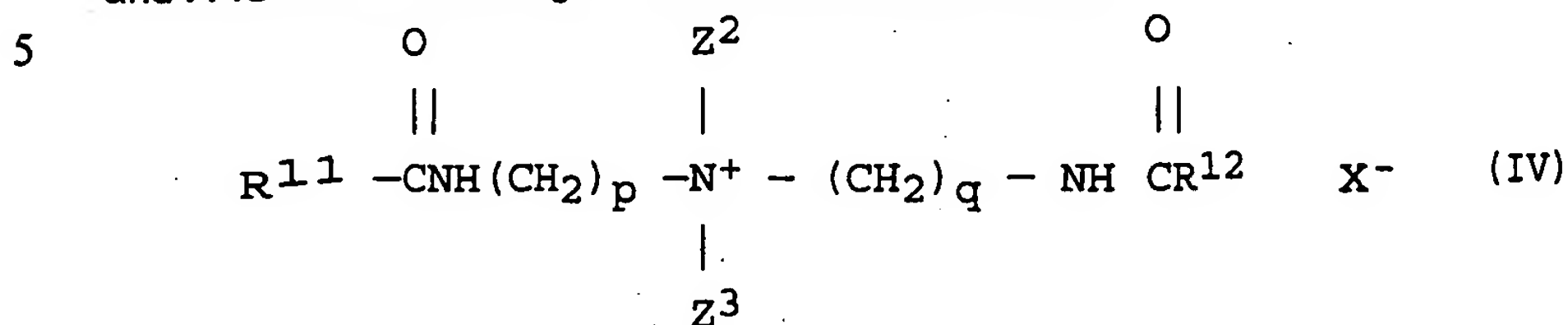
Also preferred are hydrophilically substituted cationic surfactants in which at least one of the substituents contain one or more aromatic, ether, ester, amido, or amino moieties present as substituents or as linkages in the radical chain, wherein at least one of the R<sup>1</sup> - R<sup>4</sup> radicals contain one or more hydrophilic moieties selected from alkoxy (preferably C<sub>1</sub> - C<sub>3</sub> alkoxy), polyoxyalkylene (preferably C<sub>1</sub> - C<sub>3</sub> polyoxyalkylene), alkylamido, hydroxyalkyl, alkylester, and combinations thereof. Preferably, the hydrophilically substituted cationic conditioning surfactant contains from 2 to about 10 nonionic hydrophile moieties located within the above stated ranges. Preferred hydrophilically substituted cationic surfactants include those of the formula (II) through (VII) below:



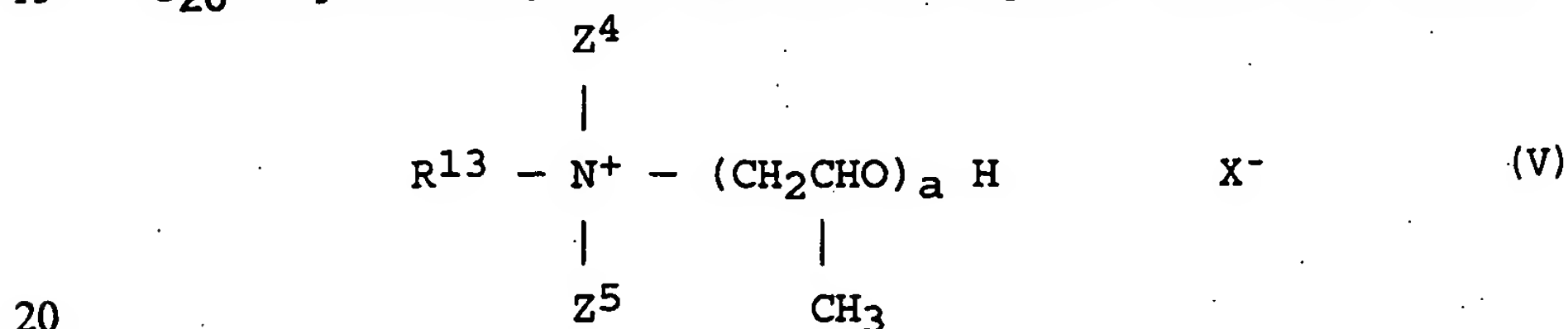
wherein n is from 8-28, x+y is from 2 to about 40, Z<sup>1</sup> is a short chain alkyl, preferably a C<sub>1</sub> - C<sub>3</sub> alkyl, more preferably methyl, or (CH<sub>2</sub>CH<sub>2</sub>O)<sub>z</sub>H wherein x+y+z is up to 60, and X is a salt forming anion as defined above;



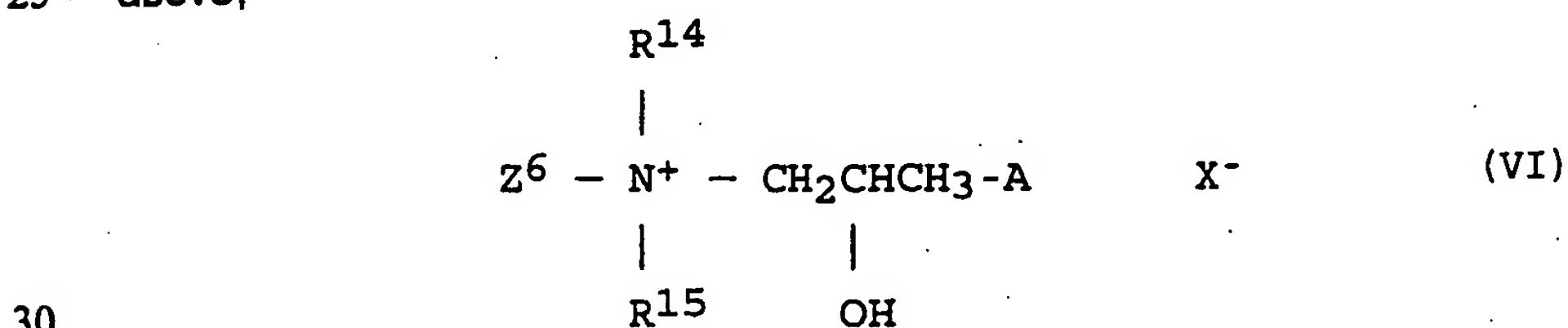
wherein  $m$  is 1 to 5, one or more of  $R^5$ ,  $R^6$ , and  $R^7$  are independently an  $C_1 - C_{30}$  alkyl, the remainder are  $CH_2CH_2OH$ , one or two of  $R^8$ ,  $R^9$ , and  $R^{10}$  are independently an  $C_1 - C_{30}$  alkyl, and remainder are  $CH_2CH_2OH$ , and  $X$  is a salt forming anion as mentioned above;



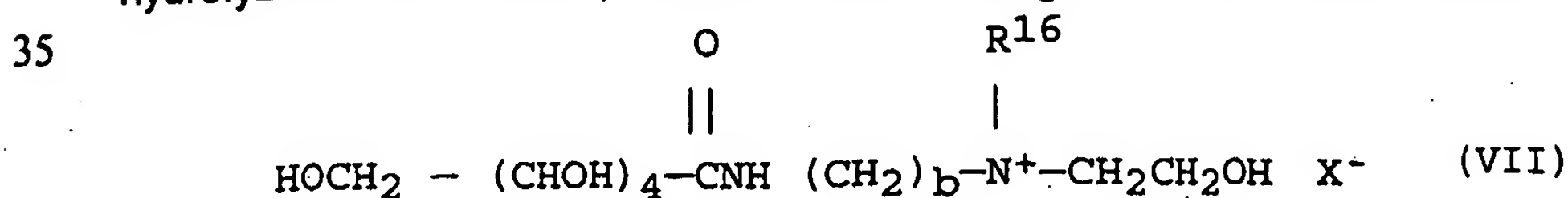
wherein  $Z^2$  is an alkyl, preferably a  $C_1 - C_3$  alkyl, more preferably methyl, and  $Z^3$  is a short chain hydroxyalkyl, preferably hydroxymethyl or hydroxyethyl,  $p$  and  $q$  independently are integers from 2 to 4, inclusive, preferably from 2 to 3, inclusive, more preferably 2,  $R^{11}$  and  $R^{12}$ , independently, are substituted or unsubstituted hydrocarbyls, preferably  $C_{12} - C_{20}$  alkyl or alkenyl, and  $X$  is a salt forming anion as defined above;



wherein  $R^{13}$  is a hydrocarbyl, preferably a  $C_1 - C_3$  alkyl, more preferably methyl,  $Z^4$  and  $Z^5$  are, independently, short chain hydrocarbyls, preferably  $C_2 - C_4$  alkyl or alkenyl, more preferably ethyl,  $a$  is from 2 to about 40, preferably from about 7 to about 30, and  $X$  is a salt forming anion as defined above;



wherein  $R^{14}$  and  $R^{15}$ , independently, are  $C_{1-3}$  alkyl, preferably methyl,  $Z^6$  is a  $C_{12}$  to  $C_{22}$  hydrocarbyl, alkyl carboxy or alkylamido, and  $A$  is a protein, preferably a collagen, keratin, milk protein, silk, soy protein, wheat protein, or hydrolyzed forms thereof; and  $X$  is a salt forming anion as defined above;





R<sup>17</sup>

wherein **b** is 2 or 3, R<sup>16</sup> and R<sup>17</sup>, independently are C<sub>1</sub> - C<sub>3</sub> hydrocarbyls preferably methyl, and X is a salt forming anion as defined above.

5 Nonlimiting examples of hydrophilically substituted cationic surfactants useful in the present invention include the materials having the following CTFA designations: quaternium-16, quaternium-61, quaternium-71, quaternium-79 hydrolyzed collagen, quaternium-79 hydrolyzed keratin, quaternium-79 hydrolyzed milk protein, quaternium-79 hydrolyzed silk, quaternium-79

10 hydrolyzed soy protein, and quaternium-79 hydrolyzed wheat protein. Highly preferred compounds include commercially available materials; VARIQUAT K1215 and 638 from Witco Chemical, MACKPRO KLP, MACKPRO WLW, MACKPRO MLP, MACKPRO NSP, MACKPRO NLW, MACKPRO WWP, MACKPRO NLP, MACKPRO SLP from McIntyre, ETHOQUAD 18/25,

15 ETHOQUAD O/12PG, ETHOQUAD C/25, ETHOQUAD S/25, and ETHODUOQUAD from Akzo, DEHYQUAT SP from Henkel, and ATLAS G265 from ICI Americas.

Salts of primary, secondary, and tertiary fatty amines are also suitable cationic surfactants. The alkyl groups of such amines preferably have from

20 about 12 to about 22 carbon atoms, and can be substituted or unsubstituted. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (with 5 moles of ethylene oxide)

25 stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate, and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic

30 amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981, which is incorporated by reference herein in its entirety.

The cationic surfactants for use herein may also include a plurality of ammonium quaternary moieties or amino moieties, or a mixture thereof.

### 35 CATIONIC SURFACTANTS

The compositions of the present invention additionally further comprise from about 0.1% to about 20% by weight, preferably from about 0.5% to

about 2% of a cationic surfactant. Cationic surfactants useful herein are the same as those useful for making the silicone emulsion as described above. The cationic surfactants used for the silicone emulsion and as a conditioning agent may or may not be the same.

- 5 In the present composition, the total amount by mole of cationic surfactants is greater than the total amount by mole of anionic surfactants. by such a balance of ionic charges within the composition, a satisfying static control benefit is achieved.

#### OTHER CONDITIONING AGENTS

- 10 Other conditioning agents known in the industry may be comprised in the present invention. Suitable conditioning agents include water soluble cationic polymers, fatty compounds, hydrocarbons, proteins, and mixtures thereof. These conditioning agents are comprised at a level of from about 0.01% to about 20% of the conditioning composition of the present invention.

#### Water Soluble Cationic Polymers

- 15 The compositions of the present invention can comprise one or more water soluble cationic polymer as a conditioning agent. By "water soluble" cationic polymer, what is meant is a polymer which is sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% in water (distilled or equivalent) at 25°C. Preferably, the polymer will be sufficiently soluble to form a substantially clear solution at 20 0.5% concentration, more preferably at 1.0% concentration.

- As used herein, the term "polymer" shall include materials whether made by polymerization of one type of monomer or made by two (i.e., copolymers) 25 or more types of monomers.

- The cationic polymers hereof will generally have a weight average molecular weight which is at least about 5,000, typically at least about 10,000, and is less than about 10 million. Preferably, the molecular weight is from about 100,000 to about 2 million. The cationic polymers will generally 30 have cationic nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, and mixtures thereof.

- The cationic charge density is preferably at least about 0.1 meq/gram, more preferably at least about 1.5 meq/gram, even more preferably at least about 1.1 meq/gram, still more preferably at least about 1.2 meq/gram. 35 Cationic charge density of the cationic polymer can be determined according to the Kjeldahl Method. Those skilled in the art will recognize that the charge density of amino-containing polymers may vary depending upon pH and the

isoelectric point of the amino groups. The charge density should be within the above limits at the pH of intended use.

Any anionic counterions can be utilized for the cationic polymers so long as the water solubility criteria is met. Suitable counterions include halides (e.g., Cl, Br, I, or F, preferably Cl, Br, or I), sulfate, and methylsulfate. Others can also be used, as this list is not exclusive.

The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other non-cationic units referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C., 1982).

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C<sub>1</sub>-C<sub>7</sub> alkyl groups, more preferably C<sub>1</sub>-C<sub>3</sub> alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol, and ethylene glycol.

The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the composition. In general, secondary and tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form, and then optionally can be converted to ammonium by a quaternization reaction. Amines can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by reaction with a salt of the formula R'X wherein R' is a short chain alkyl, preferably a C<sub>1</sub>-C<sub>7</sub> alkyl, more preferably a C<sub>1</sub>-C<sub>3</sub> alkyl, and X is an anion which forms a water soluble salt with the quaternized ammonium.

Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate,

dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions of these monomers are preferably lower alkyls such as the C<sub>1</sub>-C<sub>3</sub> alkyls, more preferably C<sub>1</sub> and C<sub>2</sub> alkyls. Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C<sub>1</sub>-C<sub>7</sub> hydrocarbyls, more preferably C<sub>1</sub>-C<sub>3</sub>, alkyls.

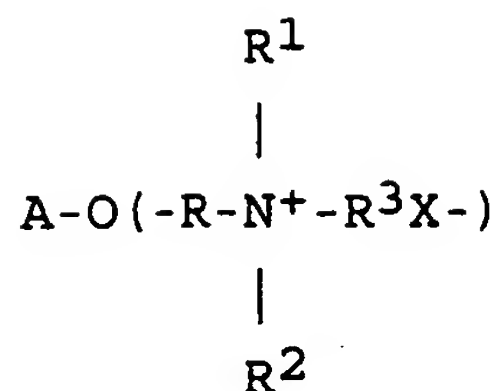
The cationic polymers hereof can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference.

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

Cationic polysaccharide polymer materials suitable for use herein include those of the formula having repeating units:

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wherein A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual, R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof, R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>) preferably being about 20 or less, and X is an anionic counterion, as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR® and LR® series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200®.

Other cationic polymers that can be used include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride (commercially available from Celanese Corp. in their Jaguar R series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g., as described in U.S. Patent 3,962,418, incorporated herein by reference), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated herein by reference.)

As discussed above, the cationic polymer hereof is water soluble. This does not mean, however, that it must be soluble in the composition. Preferably however, the cationic polymer is either soluble in the composition, or in a complex coacervate phase in the composition formed by the cationic polymer and anionic material. Complex coacervates of the cationic polymer can be formed with anionic surfactants or with anionic polymers that can optionally be added to the compositions hereof (e.g., sodium polystyrene sulfonate).



### Fatty Compounds

The compositions of the present invention can comprise one or more fatty compounds as a conditioning agent. Fatty compounds can be selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, and mixtures thereof. It is recognized that the compounds disclosed in this section of the specification can in some instances fall into more than one classification, e.g., some fatty alcohol derivatives can also be classified as fatty acid derivatives. Also, it is recognized that some of these compounds can have properties as nonionic surfactants and can alternatively be classified as such. However, a given classification is not intended to be a limitation on that particular compound, but is done so for convenience of classification and nomenclature. Nonlimiting examples of the fatty alcohols, fatty acids, fatty alcohol derivatives, and fatty acid derivatives are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, both of which are incorporated by reference herein in their entirety.

The fatty alcohols useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated. Nonlimiting examples of fatty alcohols include decyl alcohol, undecyl alcohol, dodecyl, myristyl, cetyl alcohol, stearyl alcohol, isostearyl alcohol, isocetyl alcohol, behenyl alcohol, linalool, oleyl alcohol, cholesterol, cis-4-t-butylcyclohexanol, myricyl alcohol and mixtures thereof. Especially preferred fatty alcohols are those selected from the group consisting of cetyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, and mixtures thereof.

The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Also included are diacids, triacids, and other multiple acids which meet the carbon number requirement herein. Also included herein are salts of these fatty acids. Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, arachidonic acid, oleic acid, isostearic acid, sebacic acid, and mixtures thereof. Especially preferred for use herein are the fatty



acids selected from the group consisting of palmitic acid, stearic acid, and mixtures thereof.

The fatty alcohol derivatives are defined herein to include alkyl ethers of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, esters of fatty alcohols and mixtures thereof. Nonlimiting examples of fatty alcohol derivatives include materials such as methyl stearyl ether; 2-ethylhexyl dodecyl ether; stearyl acetate; cetyl propionate; the ceteth series of compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers of cetyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; the steareth series of compounds such as steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; cetareth 1 through cetareth-10, which are the ethylene glycol ethers of cetareth alcohol, i.e. a mixture of fatty alcohols containing predominantly cetyl and stearyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; C1-C30 alkyl ethers of the ceteth, steareth, and cetareth compounds just described; polyoxyethylene ethers of branched alcohols such as octyldodecyl alcohol, dodecylpentadecyl alcohol, hexyldecyl alcohol, and iso-stearyl alcohol; polyoxyethylene ethers of behenyl alcohol; PPG ethers such as PPG-9-steareth-3, PPG-11 stearyl ether, PPG-8-ceteth-1, and PPG-10 cetyl ether; and mixtures of all of the foregoing compounds. Preferred for use herein are steareth-2, steareth-4, ceteth-2, and mixtures thereof.

The fatty acid derivatives are defined herein to include fatty acid esters of the fatty alcohols as defined above in this section, fatty acid esters of the fatty alcohol derivatives as defined above in this section when such fatty alcohol derivatives have an esterifiable hydroxyl group, fatty acid esters of alcohols other than the fatty alcohols and the fatty alcohol derivatives described above in this section, hydroxy-substituted fatty acids, and mixtures thereof. Nonlimiting examples of fatty acid derivatives include ricinoleic acid, glycerol monostearate, 12-hydroxy stearic acid, ethyl stearate, cetyl stearate, cetyl palmitate, polyoxyethylene cetyl ether stearate, polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate, ethyleneglycol monostearate, polyoxyethylene monostearate, polyoxyethylene distearate, propyleneglycol monostearate, propyleneglycol distearate, trimethylolpropane distearate, sorbitan stearate, polyglyceryl stearate, dimethyl sebacate, PEG-15 cocoate, PPG-15 stearate, glyceryl monostearate, glyceryl distearate, glyceryl

tristearate, PEG-8 laurate, PPG-2 isostearate, PPG-9 laurate, and mixtures thereof. Preferred for use herein are glycerol monostearate, 12-hydroxy stearic acid, and mixtures thereof.

Highly preferred fatty compounds are cetyl alcohol, stearyl alcohol, and mixtures thereof.

#### Hydrocarbons

Hydrocarbons are useful herein as conditioning agents. Useful hydrocarbons include straight chain, cyclic, and branched chain hydrocarbons which can be either saturated or unsaturated. The hydrocarbons preferably will have from about 12 to about 40 carbon atoms, more preferably from about 12 to about 30 carbon atoms, and most preferably from about 12 to about 22 carbon atoms. Also encompassed herein are polymeric hydrocarbons of alkenyl monomers, such as polymers of C2-C6 alkenyl monomers. These polymers can be straight or branched chain polymers. The straight chain polymers will typically be relatively short in length, having a total number of carbon atoms as described above in this paragraph. The branched chain polymers can have substantially higher chain lengths. The number average molecular weight of such materials can vary widely, but will typically be up to about 500, preferably from about 200 to about 400, and more preferably from about 300 to about 350. Also useful herein are the various grades of mineral oils. Mineral oils are liquid mixtures of hydrocarbons that are obtained from petroleum. Specific examples of suitable hydrocarbon materials include paraffin oil, mineral oil, dodecane, isododecane, hexadecane, isohexadecane, eicosene, isoeicosene, tridecane, tetradecane, polybutene, polyisobutene, and mixtures thereof. Isododecane, isohexadecane, and isoeicosene are commercially available as Permethyl 99A, Permethyl 101A, and Permethyl 1082, from Presperse, South Plainfield, NJ. A copolymer of isobutene and normal butene is commercially available as Indopol H-100 from Amoco Chemicals. Preferred for use herein are hydrocarbon conditioning agents selected from the group consisting of mineral oil, isododecane, isohexadecane, polybutene, polyisobutene, and mixtures thereof.

#### ADDITIONAL SURFACTANTS

Hair conditioning compositions of the present invention may further comprise additional surfactants. Such additional surfactants comprise amphoteric surfactants, zwitterionic surfactants, nonionic surfactants, and mixtures thereof which do not affect the conditioning composition of the

present invention. These may or may not be the same surfactants comprised in the silicone emulsion as mentioned above.

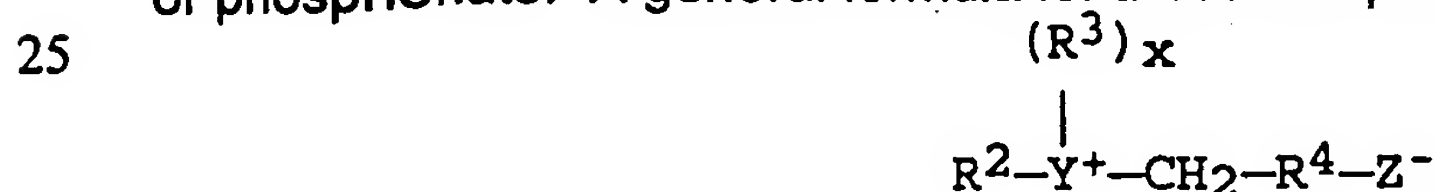
The additional surfactant is particularly useful for compositions in the form of spray or mousse, wherein the additional surfactant is used to suspend the conditioning agents and other components which are insoluble in water. Additional surfactants are typically included at a level by weight of from about 0.1% to about 15%, preferably from about 0.3% to about 10% of the composition. The level and species are selected according to the compatibility with other components, and desired characteristic of the product.

#### Amphoteric and Zwitterionic Surfactants

The compositions of the present invention can comprise amphoteric and/or zwitterionic surfactants.

Amphoteric surfactants for use herein include the derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical is straight or branched and one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

Zwitterionic surfactants for use herein include the derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals are straight or branched, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



where  $R^2$  contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms;  $R^3$  is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom;  $R^4$  is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

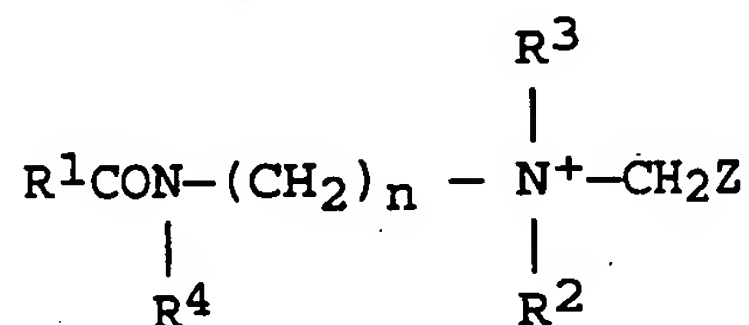
Examples of amphoteric and zwitterionic surfactants also include sultaines and amidosultaines. Sultaines, including amidosultaines, include

for example, cocodimethylpropylsultaine, stearyldimethylpropylsultaine, lauryl-bis-(2-hydroxyethyl) propylsultaine and the like; and the amidosultaines such as cocamidodimethylpropylsultaine, stearylamidodimethylpropylsultaine, laurylamidobis-(2-hydroxyethyl) propylsultaine, and the like. Preferred are amidohydroxysultaines such as the C<sub>12</sub>-C<sub>18</sub> hydrocarbyl amidopropyl hydroxysultaines, especially C<sub>12</sub>-C<sub>14</sub> hydrocarbyl amido propyl hydroxysultaines, e.g., laurylamidopropyl hydroxysultaine and cocamidopropyl hydroxysultaine. Other sultaines are described in U.S. Patent 3,950,417, which is incorporated herein by reference in its entirety.

Other suitable amphoteric surfactants are the aminoalkanoates of the formula  $R-NH(CH_2)_nCOOM$ , the iminodialkanoates of the formula  $R-N[(CH_2)_mCOOM]_2$  and mixtures thereof; wherein n and m are numbers from 1 to about 4, R is C<sub>8</sub> - C<sub>22</sub> alkyl or alkenyl, and M is hydrogen, alkali metal, alkaline earth metal, ammonium or alkanolammonium.

Examples of suitable aminoalkanoates include n-alkylamino-propionates and n-alkyliminodipropionates, specific examples of which include N-lauryl-beta-amino propionic acid or salts thereof, and N-lauryl-beta-imino-dipropionic acid or salts thereof, and mixtures thereof.

Other suitable amphoteric surfactants include those represented by the formula :



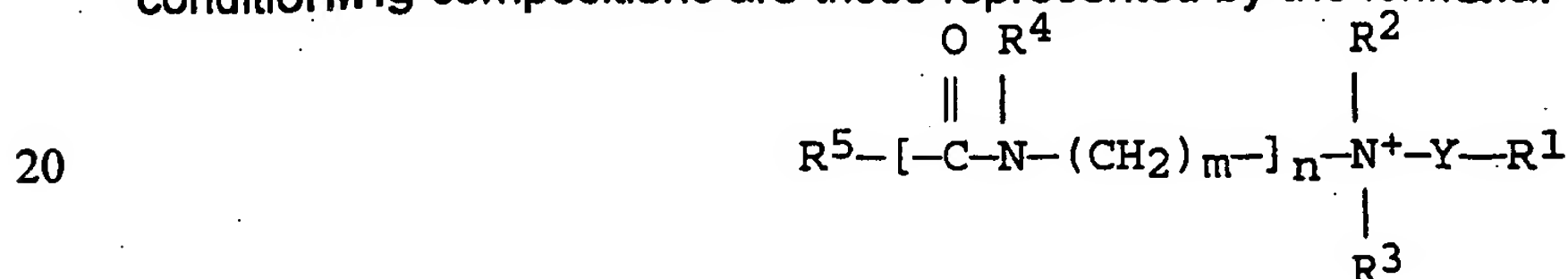
wherein R<sup>1</sup> is C<sub>8</sub> - C<sub>22</sub> alkyl or alkenyl, preferably C<sub>12</sub>-C<sub>16</sub>, R<sup>2</sup> and R<sup>3</sup> is independently selected from the group consisting of hydrogen, CH<sub>2</sub>CO<sub>2</sub>M, CH<sub>2</sub>CH<sub>2</sub>OH, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOM, or (CH<sub>2</sub>CH<sub>2</sub>O)<sub>m</sub>H wherein m is an integer from 1 to about 25, and R<sup>4</sup> is hydrogen, CH<sub>2</sub>CH<sub>2</sub>OH, or CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOM, Z is CO<sub>2</sub>M or CH<sub>2</sub>CO<sub>2</sub>M, n is 2 or 3, preferably 2, M is hydrogen or a cation, such as alkali metal (e.g., lithium, sodium, potassium), alkaline earth metal (beryllium, magnesium, calcium, strontium, barium), or ammonium. This type of surfactant is sometimes classified as an imidazoline-type amphoteric surfactant, although it should be recognized that it does not necessarily have to be derived, directly or indirectly, through an imidazoline intermediate. Suitable materials of this type are marketed under the tradename MIRANOL and are understood to comprise a complex mixture

of species, and can exist in protonated and non-protonated species depending upon pH with respect to species that can have a hydrogen at R<sup>2</sup>. All such variations and species are meant to be encompassed by the above formula.

5        Examples of surfactants of the above formula are monocarboxylates and dicarboxylates. Examples of these materials include cocoamphocarboxypropionate, cocoamphocarboxypropionic acid, cocoamphocarboxyglycinate (alternately referred to as cocoamphodiacetate), and cocoamphoacetate.

10       Commercial amphoteric surfactants include those sold under the trade names MIRANOL C2M CONC. N.P., MIRANOL C2M CONC. O.P., MIRANOL C2M SF, MIRANOL CM SPECIAL (Miranol, Inc.); ALKATERIC 2CIB (Alkaril Chemicals); AMPHOTERGE W-2 (Lonza, Inc.); MONATERIC CDX-38, MONATERIC CSH-32 (Mona Industries); REWOTERIC AM-2C (Rewo Chemical Group); and SCHERCOTERIC MS-2 (Scher Chemicals).

15       Betaine surfactants, i.e. zwitterionic surfactants, suitable for use in the conditioning compositions are those represented by the formula:



wherein: R<sup>1</sup> is a member selected from the group consisting of  
COOM and CHCH<sub>2</sub>SO<sub>3</sub>M

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30       R<sup>2</sup> is lower alkyl or hydroxyalkyl; R<sup>3</sup> is lower alkyl or hydroxyalkyl; R<sup>4</sup> is a member selected from the group consisting of hydrogen and lower alkyl; R<sup>5</sup> is higher alkyl or alkenyl; Y is lower alkyl, preferably methyl; m is an integer from 2 to 7, preferably from 2 to 3; n is the integer 1 or 0; M is hydrogen or a cation, as previously described, such as an alkali metal, alkaline earth metal, or ammonium. The term "lower alkyl" or "hydroxyalkyl" means straight or branch chained, saturated, aliphatic hydrocarbon radicals and substituted hydrocarbon radicals having from one to about three carbon atoms such as, for example, methyl, ethyl, propyl, isopropyl, hydroxypropyl, hydroxyethyl, and the like. The term "higher alkyl or alkenyl" means straight or branch chained saturated (i.e., "higher alkyl") and unsaturated (i.e., "higher alkenyl") aliphatic hydrocarbon radicals having from about eight to about 20 carbon atoms such as, for example, lauryl, cetyl, stearyl, oleyl, and the like. It should



be understood that the term "higher alkyl or alkenyl" includes mixtures of radicals which may contain one or more intermediate linkages such as ether or polyether linkages or non-functional substituents such as hydroxyl or halogen radicals wherein the radical remains of hydrophobic character.

5        Examples of surfactant betaines of the above formula wherein n is zero which are useful herein include the alkylbetaines such as cocodimethylcarboxymethylbetaine, lauryldimethylcarboxymethylbetaine, lauryldimethyl-alpha-carboxyethylbetaine, cetyltrimethylcarboxymethylbetaine, lauryl-bis-(2-hydroxyethyl)carboxymethylbetaine, stearyl-bis-(2-hydroxyethyl)carboxymethylbetaine, hydroxypropyl)carboxymethylbetaine, oleyldimethyl-gamma-carboxypropylbetaine, lauryl-bis-(2-hydroxypropyl)alpha-carboxyethylbetaine, etc. The sulfobetaines may be represented by cocodimethylsulfopropylbetaine, stearyltrimethylsulfopropylbetaine, lauryl-bis-(2-hydroxyethyl)sulfopropylbetaine, and the like.

15        Specific examples of amido betaines and amidosulfo betaines useful in the conditioning compositions include the amidocarboxybetaines, such as cocamidodimethylcarboxymethylbetaine, laurylamidodimethylcarboxymethylbetaine, cetyltrimethylcarboxymethylbetaine, laurylamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, cocamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, etc. The amido sulfobetaines may be represented by cocamidodimethylsulfopropylbetaine, stearyltrimethylsulfopropylbetaine, laurylamido-bis-(2-hydroxyethyl)-sulfopropylbetaine, and the like.

#### Nonionic Surfactants

25        The compositions of the present invention can comprise a nonionic surfactant. Nonionic surfactants include those compounds produced by condensation of alkylene oxide groups, hydrophilic in nature, with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature.

30        Preferred nonlimiting examples of nonionic surfactants for use herein include the following:

35        (1) polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 20 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in



amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol;

(2) those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products;

(3) condensation products of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configurations, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms;

(4) long chain tertiary amine oxides of the formula  $[R^1R^2R^3N \rightarrow O]$  where  $R^1$  contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and  $R^2$  and  $R^3$  contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals;

(5) long chain tertiary phosphine oxides of the formula  $[RR'R''P \rightarrow O]$  where R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties and  $R'$  and  $R''$  are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms;

(6) long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties;

(7) alkyl polysaccharide (APS) surfactants (e.g. alkyl polyglycosides), examples of which are described in U.S. Patent 4,565,647, which is incorporated herein by reference in its entirety, and which discloses APS surfactants having a hydrophobic group with about 6 to about 30 carbon atoms and a polysaccharide (e.g., polyglycoside) as the hydrophilic group; optionally, there can be a polyalkylene-oxide group joining the hydrophobic and hydrophilic moieties; and the alkyl group (i.e., the hydrophobic moiety) can be saturated or unsaturated, branched or unbranched, and unsubstituted or substituted (e.g., with hydroxy or cyclic rings); a preferred material is alkyl

polyglucoside which is commercially available from Henkel, ICI Americas, and Seppic; and

(8) polyoxyethylene alkyl ethers such as those of the formula  $RO(CH_2CH_2)_nH$  and polyethylene glycol (PEG) glyceryl fatty esters, such as those of the formula  $R(O)OCH_2CH(OH)CH_2(OCH_2CH_2)_nOH$ , wherein n is from 1 to about 200, preferably from about 20 to about 100, and R is an alkyl having from about 8 to about 22 carbon atoms.

#### OPTIONAL COMPONENTS

A wide variety of additional ingredients can be formulated into the present composition. These include: other conditioning agents such as hydrolysed collagen, hydrolysed keratin, proteins, plant extracts, and nutrients; hair-hold polymers; other surfactants such as anionic surfactants; additional thickening agents and suspending agents such as xanthan gum, guar gum, hydroxyethylcellulose, methylcellulose, starch and starch derivatives; viscosity modifiers such as methanolamides of long chain fatty acids such as cocomonoethanol amide; pearlescent aids such as ethylene glycol distearate; preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; solvents such as polyvinyl alcohol, ethyl alcohol and volatile and non-volatile silicone fluids of low molecular weight; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents such as the thioglycolates; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; and polymer plasticizing agents, such as glycerin, disobutyl adipate, butyl stearate, and propylene glycol; and ultraviolet and infrared screening and absorbing agents such as octyl salicylate, and propellants such as LPG gas. Such optional ingredients generally are used individually at levels from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0% by weight of the composition.

#### EXAMPLES

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing

from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA name, or otherwise defined below.

### Examples I - III

The components shown below can be prepared by any conventional method well known in the art. A suitable method is as follows: Stearyltrimethylammonium chloride, Steareth-20, and preservatives are added into distilled water under agitation at 70 - 75 C°. Other ingredients except for silicone emulsion and perfume are added to the above and agitated. The obtained mixture is allowed to cool, and the silicone emulsion and perfume is added. The obtained composition is packed into packages equipped with a spraying device to make a conditioning spray.

COMPONENTS		AMOUNT (%)		
	Example No.	I	II	III
	Silicone Emulsion 1 *1	9.0	-	-
15	Silicone Emulsion 2 *2	-	9.0	6.4
	Stearyltrimethyl ammonium chloride	0.3	0.3	0.3
	Steareth-20	0.3	0.3	0.3
	Na4 EDTA	0.14	0.14	0.14
	Citric acid	0.06	0.06	0.06
20	Preservative	0.9	0.9	0.9
	Perfume	0.04	0.04	0.04
	DI Water	q.s.to make 100		

\*1 Silicone Emulsion 1: An emulsion of the following formula:

	33%	dimethiconol
25	5.4%	cyclomethicone
	0.8%	sodium dodecylbenzene sulfonate
	1.6%	POE(18) nonyl phenyl ether
	0.8%	cetyltrimethyl ammonium chloride
	0.45%	preservative
30	57.95%	water

The dimethiconol included has an average molecular weight of about 280,000 with average particle size of about 160nm, and the level to the entire composition is 3.0% for Example I.

\*2 Silicone Emulsion 2: An emulsion of the following formula:

35	33%	dimethiconol
	5.4%	cyclomethicone
	0.8%	sodium dodecylbenzene sulfonate

1.6% POE(18) nonyl phenyl ether  
0.8% cetyltrimethyl ammonium chloride  
0.45% preservative  
57.95% water

- 5 The dimethiconol included has an average molecular weight of about 270,000 with average particle size of about 160nm, and the level to the entire composition are 3.0% and 2.1% for Examples II and III, respectively.

What is claimed is:

1. A hair conditioning composition comprising by weight:

(a) a silicone emulsion comprising:

- 5 i) from about 0.01% to about 20% of the entire composition a silicone polymer selected from the group consisting of a polyalkyl siloxane having a molecular weight of at least 20,000, a polyaryl siloxane having a molecular weight of at least 20,000, an amino-substituted siloxane having a molecular weight of at least 5,000, a silicone resin having a molecular weight of at least 5,000, and mixtures thereof;
- 10 ii) an anionic surfactant;
- iii) a compatibilizing surfactant; and
- iv) a cationic surfactant;

wherein the silicone polymer is dispersed as a particle having an average size of not more than about 450 nm;

(b) from about 0.1% to about 20% of a cationic surfactant; and

15 (c) water;

wherein the total amount by mole of cationic surfactants in the composition is greater than the total amount by mole of anionic surfactants in the composition.

2. The hair conditioning composition according to Claim 1 wherein the silicone polymer is selected from the group consisting of a polyalkyl siloxane having a molecular weight of at least 200,000, a polyaryl siloxane having a molecular weight of at least 200,000, an amino-substituted siloxane having a molecular weight of at least 10,000, a silicone resin having a molecular weight of at least 10,000, and mixtures thereof.

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3. The hair conditioning composition according to Claim 1 wherein the silicone polymer is an amodimethicone having a molecular weight of at least 10,000.

4. The hair conditioning composition according to Claim 1 wherein the silicone emulsion comprises the silicone polymer dispersed as a particle having an average size of from about 150nm to about 250nm.

5. The hair conditioning composition according to any of Claims 1 through 4 wherein the composition is in the form of a spray or mousse further comprising an additional surfactant selected from the group consisting of nonionic surfactants, amphoteric surfactants, zwitterionic surfactants, and mixtures thereof.



# INTERNATIONAL SEARCH REPORT

Intern. Application No  
PCT/US 96/17521

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 23581 A (PROCTER & GAMBLE) 8 September 1995 see the whole document -----	1-5

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

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- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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- \*P\* document published prior to the international filing date but later than the priority date claimed

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- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

11 September 1997

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		CA 2184169 A	08-09-95
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